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(54) **Photostimulable luminescence glass composition**

(57) A photostimulable luminescence glass composition including active cations which release light having a wavelength in the blue-colour or ultraviolet region when those parts of the glass which have been stimulated by radiation such as X-rays, γ-rays, α-rays, β-rays, electron beams, neutron beams, ion beams, ultra-violet rays having an energy equal to or greater than the band gap of the glass, etc.. are excited by visible or infra-red light. Ce^{3+}, Eu^{2+} etc. can be used as the active cation, and are preferably included in an amount of 10 mole% or less of all the cations, and particularly preferably in an amount in the range of 0.001 to 2 mole%. A silicate glass, a borate glass, a phosphate glass, a mixed oxide glass based on a mixture the above, a halide glass, a halogen phosphate glass etc. are used as the basic glass.

The photostimulable luminescence glass composition has practical durability and mechanical strength and is suited to the recording and playback of radiation images.

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Description

The present invention relates to a photostimulable luminescence glass composition used in radiation dose meters, radiation image conversion panels etc. which work on photostimulable luminescence, and also relates to recording and playback of radiation images using photostimulable luminescence glass.

In X-ray sensitized paper and image intensifiers, phosphors which generate luminescence in response to the dose of X-rays absorbed by it are used. In order to reduce the dose of radiation to which, for example, a patient or user of a X-ray related device is exposed to, there have been demands for the development of a phosphor which generates good luminescence even upon minute doses of X-ray exposure, i.e. which is highly sensitive to X-rays.

The radiation image conversion method is known as a method which can be used instead of radiography which uses silver salts. In this method, a phosphor is made to absorb radiation which has passed through an object, and then this phosphor is excited with a certain type of energy to cause the radiation energy stored in the phosphor to be released as luminescence. For example, a panel having a layer of a photostimulable luminescence phosphor formed on a support such as paper is used, and visible light radiation and infra-red radiation is used as the excitation energy.

The radiation image conversion method which is disclosed in Japanese Patent Application Publication No. Sho 59-75200 and employs $BaFX;Eu^{2+}$ (X:Cl,Br,I) as the photostimulable luminescence phosphor, has the following excellent features and has started to be used in a wide range of fields such as medical science, medical treatment, medicine, bioscience, high energy, mining etc..

(1) Has a sensitivity from tens to hundreds of times as high as that of photographic film; stored noise can be eliminated before use; low noise.
(2) With respect to photostimulated luminescence, it linearly responds to doses of radiation in a wide range of five figures, has a wide dynamic range and has excellent linearity.
(3) Has wide sensitive area; high resolution.
(4) Can easily be connected to a computer whereby a direct digital image signal can be obtained during the reading process, thereby facilitating storage and retrieval.
(5) Can be used repeatedly.

However, in the case of phosphors such as $BaFX;Eu^{2+}$, the process of production thereof is extremely complicated, the number of production process steps is large, and the time required for production is long, making them extremely costly. Furthermore, due to the fact that they are generally synthesized in the solid phase at temperatures around 1000°C, there is a tendency for the particles to agglomerate. As a result, in order to increase the fluorescent strength, crushing and classification has to be carried out during the stage of after-treatment to obtain, to a great extent as possible, particles all having a same suitable size, and this results in a reduced yield. Furthermore, methods of depositing or applying coatings of the phosphor in it's powder form onto a substrate are used in order to form a fluorescent sheet, and due to the fact that powders have multi-faced shapes, the surface of the sheet becomes pitted with the result that fine control processes were deemed necessary in order to provide a uniform film, and even then the formation of a uniform film was almost impossible. Furthermore, due to the fact that the powder particles are relatively roughly packed together, and that the surface has a pitted shape, the fluorescence generated by excitation is repeatedly scattered between the phosphor particles with the result that the amount of light passing through the front face of the fluorescent sheet was reduced. Consequently, the sensitivity was reduced, the uniformity of sensitivity was poor, and it was impossible to increase the resolution beyond a certain critical value.

On the other hand, there have also been developed glass dosimeters which detect radiation such as X-rays. The main types are type I(for example, SiO_2-B_2O_3-Na_2O-Al_2O_3 system glass containing Co^{2+}; Mn^{2+}-Fe^{3+}-containing glass; $Mg(PO_3)_2$ glass; Sb_2O_3 system glass; Bi_2O_3 containing glass; phosphate glass containing Ag etc.), which use the phenomenon in which the glass becomes coloured by exposure to radiation; type II (Li_2O-Al_2O_3-SiO_2 glass containing Tb^{3+}; phosphate glass containing Mn etc.) which work on the fact that trap centres generated by exposure to radiation fluorescently emit light when heated and then disappear; and type III (phosphate glass containing Ag etc.) which work on radiophoto luminescence.

With type I, the range of doses which can be measured is narrow, and playback by heating is not complete. Furthermore, Sb_2O_3 system glasses and Bi_2O_3-containing glasses are difficult to produce stably.

With type II which work on thermo-luminescence, the sensitivity is low and there is the problem of deformation upon heating. Furthermore, it is impossible to substantially measure the dose distribution of radiation such as X-rays etc..

Type III work on the phenomenon of radiophotoluminescence in which orange-coloured fluorescence is emitted when Ag-containing phosphate glass is exposed to radiation such as X-rays and then stimulated with ultra-violet light having a wavelength of about 360nm. By measuring the amount of fluorescence generated by this phenomenon, it is possible to determine how much radiation the glass was exposed to. The electrons generated by the exposure to radiation are trapped by Ag^+ whereby Ag^+ is converted into Ag^0, and the positive holes are trapped by the PO_4 tetrahedrons which make up the network of the phosphate glass. With time, the positive holes transfer to Ag^+ whereby Ag^{2+} centres are generated. This is known as build-up

of radiophoto-luminescence. The speed thereof will depend on the composition of the glass, but even in the case of the fastest glasses, it takes tens of minutes, and with some glasses it takes a number of days. As a result, it is impossible to measure radiation doses or synthesize images in a short period of time. In addition, the dynamics range is narrow and the operability is poor.

The present invention was realised in order to solve these kinds of problems. Through the exploitation of the characteristics of glass such as uniformity and its capability to be polished to high precision, and through the incorporation of Ce^{3+}, Eu^{2+} etc. as active cations for photostimulated luminescence in the glass composition, the present invention has as its objective highly reliable recording and playback of radiation images using a photostimulable luminescence glass which has practical durability and mechanical strength, does not exhibit the direction dependency with respect to light emission observed with crystals, and has good formability and uniformity of sensitivity.

In order to realise this objective, the photostimulable luminescence glass composition of the present invention is a glass which includes active cations which emit light of a wavelength in the ultraviolet or blue-colour region when parts thereof which have been exposed to radiation such as X-rays, γ-rays, α-rays, β-rays, electron beams, neutron beams, ion beams and ultraviolet rays having an energy equal to or greater than the bandgap of glass, are excited by visible light or infra-red light. When Ce^{3+}, Eu^{2+} etc. are used as the active cations, they are included in a total amount of 10 mole% or less on the basis of all of the cations, and preferably in an amount in the range of 0.001 to 2 mole%. As the glass, a silicate glass, a borate glass, a phosphate glass, a mixed oxide glass based on a mixture thereof, a halide glass or a halogen phosphate glass may be used.

In the case of an oxide glass, it is preferable that the photostimulable luminescence glass composition of the present invention includes, as cations which comprise the glass, 30 to 99 mole% (preferably 45 to 95 mole%) of at least one of Si^{4+}, B^{3+} and P^{5+}, 0 to 70 mole% (preferably 5 to 60 mole%) of at least one of Li^+, Na^+, K^+, Rb^+, Cs^+ and Tl^+, 0 to 70 mole% (preferably 0 to 40 mole%) of at least one of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}, 0 to 30 mole% (preferably 0 to 10 mole%) of Al^{3+}, and 0 to 40% (preferably 0 to 30 mole%) of at least one of Y^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, Bi^{3+} and Ln^{3+} (where Ln is a rare earth element other than Ce), wherein the percentages are based on the total of all cations.

In the case of a halide glass, it is preferable that the glass has a composition including, as the cations which comprise the glass, 10 to 60 mole% (preferably 20 to 40 mole%) of Al^{3+}, 8 to 70 mole% (preferably 8 to 60 mole%) of at least one of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}, 0 to 30 mole% (preferably 0 to 25 mole%)of at least one of Y^{3+} and Ln^{3+} (wherein Ln is a rare earth element other than Ce), 0 to 20 mole% (preferably 0 to 15 mole%)of Hf^{4+} and 0 to 20 mole% (preferably 0 to 10 mole%) of at least one of Li^+, Na^+ and K^+, wherein the percentages are based on the total of all cations, and including, as anions which comprise the glass, 0 to 20 mole% (preferably 0 to 10 mole%) of Cl^-, and 80 to 100 mole% (preferably 90 to 100 mole%) of F^-, wherein the percentages are based on the total of all anions.

In the case of a halogen phosphate glass, it is preferable that the glass has a composition including, as the cations which comprise the glass, 10 to 60 mole% (preferably 20 to 40 mole%) of Al^{3+}, 0.1 to 80 mole% (preferably 5 to 60 mole%) of P^{5+}, 8 to 70 mole% (preferably 8 to 60 mole%) of at least one of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}, 0 to 30 mole% (preferably 0 to 25 mole%) of at least one of Y^{3+} and Ln^{3+} (wherein Ln is a rare earth element other than Ce), 0 to 20 mole% (preferably 0 to 15 mole%) of Hf^{4+} and 0 to 20 mole% (preferably 0 to 10 mole%) of at least one of Li^+, Na^+ and K^+, wherein the percentages are based on the total of all cations, and including, as anions which comprise the glass, 1 to 95 mole% (preferably 1 to 50 mole%) of O^{2-}, 0 to 20 mole% (preferably 0 to 10 mole%) of Cl^- and 5 to 99 mole% (preferably 40 to 99 mole%) of F^-, wherein the percentages are based on the total of all anions.

The batch composed to give a glass having the desired composition, is then melted and shaped either in an reducing atmosphere or after addition of a reducing agent. The molten glass composition may then be formed into a flat sheet, a curved face or fibers. Glass fibers may be further bundled together to form a microchannel plate having a flat structure.

The photostimulable luminescence glass is made to absorb radiation or radiation which has been passed through an object, whereafter it is irradiated by visible light or infra-red light to cause it to release the energy held by it in the form of ultra-violet or blue-colour fluorescence. Recording and playback is carried out by detecting the fluorescence with fluorescence detecting means.

If photostimulable luminescence glass including Ce^{3+} is exposed to irradiation such as X-rays having an energy greater than the bandgap of glass, pairs of electrons and positive holes are generated in the glass. The electrons are trapped by defects existing in the glass, to form, for example, F-centres. The positive holes are trapped by the Ce^{3+}. The energy level of both of these trap centres lies between the valence band and conduction band of glass, and since the depth thereof is relatively deep, they exist stably at room temperatures. This state corresponds to the state in which the image is stored, i.e. the state in which the image is recorded.

The glass is then irradiated by a He-Ne laser (wavelength 633nm), a YAG laser (wavelength 1.06μm) or visible light having an energy corresponding to the difference in energy between the ground state and the excited state of the electron trap centres, whereby the electrons of the F-centres are stimulated and released, and recombine with the positive holes trapped by the positive hole trap centres Ce^{3+}. The energy of this

recombination causes light emitting centres situated right close by to become excited to an excited state, and when these return to the ground state they give out an ultra-violet or blue-colour light. The intensity of the light emitted is proportional to the dose of exciting radiation to which the glass was exposed at the beginning, and thus the dose of radiation can be measured by measuring the intensity of the light emitted.

Eu^{2+}-containing glass also emits fluorescence through stimulation by a similar mechanism to that discussed above for Ce^{3+}.

As described above, the stimulation-emission glass of the present invention includes, as an active cation, at least one of Ce^{3+} and Eu^{2+}. Excitation with radiation such as X-rays, γ-rays, α-rays, β-rays, electron beams, ultra-violet rays having an energy greater than the band gap of the glass, neutron beams, ion beams causes the formation of trap centres which have an energy level between the valence electron band and conduction band of the glass, and which exist stably at room temperature. As a result, it is possible to produce radiation dosimeters and radiation image conversion panels with which the measurement of exposure doses and the synthesis of images can be carried out in a short time. Furthermore, since it has excellent glass formability and thus can be easily formed into various forms such as sheets, rods and fibers etc., it may be used as a photostimulable luminescence phosphor having practical durability and mechanical strength.

Figure 1 shows a system for measuring stimulation emission spectra
Figure 2 shows a system for measuring stimulation-excitation spectra
Figure 3 shows the stimulation-excitation spectra of Example 1.
Figure 4 shows the afterglow characteristics of Examples 1 and 2.

The photostimulable luminescence glass composition of the invention shall now be described in more detail with reference to preferred embodiments thereof.

The photostimulable luminescence glass composition of the present invention includes active cations such as Ce^{3+}, Eu^{2+} etc. as cations essential for the trapping of the positive holes generated by excitation with radiation such as X-rays, γ-rays, α-rays, β-rays, electron beams, neutron beams, ion beams and ultraviolet rays having an energy equal or greater than the band gap of the glass. It is preferred that the concentration of the active cations is set to be 10 mole % or less of all the cations which comprise the glass, and further preferred that it is set to be in the range of 0.001 to 2 mole%. If the concentration of active cations is too low, then it becomes impossible to trap almost any of the positive holes generated by the excitation with radiation. Conversely, if the concentration is too high, then clusters such as Ce^{3+}-O-Ce^{3+} are formed, whereby concentration quenching due to energy transfer etc. tends to occur, with the result that the strength of the fluorescence is decreased.

Silicate glass, borate glass, phosphate glass, a mixed oxide glass such as a mixture of the above, a halide glass or a halogen phosphate glass may be used as the glass. In the case that the photostimulable luminescence glass composition is an oxide glass, it is preferable that the glass includes 30 to 99% of at least one of Si^{4+}, B^{3+} and P^{5+} as cations which form the glass network. If the total amount of Si^{4+}, B^{3+} and P^{5+} is less than 30 mole%, then the formability of the glass is poor, and it tends to crystallize. On the other hand, if the total concentration of Si^{4+}, B^{3+} and P^{5+} exceeds 99 mole%, defects, which trap the electrons, are not easily formed in the glass. Furthermore, if the concentration of Si^{4+} is greater than 99 mole%, it becomes difficult to prepare the glass using the conventional melting process. If the total concentration of B^{3+} and P^{5+} is greater than 99 mole%, the chemical durability of the glass is decreased. When taking into consideration both the stability with respect to crystallization and the thermal stability of the glass which is required for the shaping thereof, it is preferable that the total amount of Si^{4+}, B^{3+} and P^{5+} is in a range from 45 to 95 mole%.

0 to 70 mole% of at least one of Li^+, Na^+, K^+, Rb^+, Cs^+ and Tl^+ should be included as cations which modify the glass network. As the amount of Li^+, Na^+, K^+, Rb^+, Cs^+ and Tl^+ in the glass increases, the number of defects which can trap electrons increases, with the result that F-centres etc. are more easily generated in the glass upon exposure thereof to radiation. However, if the total concentration of Li^+, Na^+, K^+, Rb^+, Cs^+ and Tl^+ exceeds 70 mole%, then the formability of glass is poor. It is more preferable that the total concentration of Li^+, Na^+, K^+, Rb^+, Cs^+, Tl^+ etc. is in a range of 5 to 60 mole%.

Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} are cations which act to modify the glass network. As the amount of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+} or Zn^{2+} in the glass increases, in particular as Ba^{2+} with a large atomic weight increases, the glass efficiently absorbs radiation, and the energy thereof is trapped and held by defects. Also, when the energy of the radiation is released by excitation with visible or infra-red light, the photostimulated luminescence is detected with high sensitivity. However, if the total concentration of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} exceeds 70 mole%, then the glass-forming ability is deteriorated. It is particularly preferred that the total concentration of the Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} is in a range of 0 to 40 mole%.

Al^{3+} is a cation which functions to form the glass network. As the amount of Al^{3+} in the glass increases, the durability, mechanical strength of the glass are improved. However if the concentration of the Al^{3+} exceeds 30 mole%, the proportion of Al^{3+} existing in the glass as AlO_4 increases, and since AlO_4 traps positive holes, there is the fear that the fluorescence emitted by stimulation will be weakened. It is particularly preferable

that the concentration of Al^{3+} is in a range of 0 to 10 mole%.

Y^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, Bi^{3+} and Ln^{3+} (Ln is a rare earth element other than Ce) are also cations which act to modify the glass network. As the amount of Y^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, Bi^{3+}, Ln^{3+} increases, X-rays are absorbed by the glass more efficiently, and the energy thereof is trapped and held by the defects. However, if the total concentration of Y^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, Bi^{3+} and Ln^{3+} exceeds 40 mole%, the glass-forming ability becomes poor. It is particularly preferred that the total concentration of Y^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, Bi^{3+}, Ln^{3+} is in a range of 0 to 30 mole%.

In the case that the photostimulable luminescence glass composition is a halide glass, it is preferred that it contain 10 to 60 mole% of Al^{3+} as cations which form the glass network. If the content of Al^{3+} is less than 10 mole% or greater than 60 mole%, the glass tends to crystallize. It is particularly preferred that the content of Al^{3+} is in the range of 20 to 40 mole%.

It is preferred that the glass contains 8 to 70 mole% of at least one of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} as divalent modifying ions which have the action of complementing the network structure of the glass. If the content of the divalent modifying ions is less than 8 mole% or greater than 70 mole%, then the glass tends to crystallize. It is particularly preferred that the content of divalent modifying ions is in a range of 8 to 60 mole%.

It is preferred that the glass contains 0 to 30 mole% of at least one of Y^{3+} and Ln^{3+} (wherein Ln is a rare earth element other than Ce) as trivalent modifying ions which have the action of complementing the network structure of the glass. If the content of the trivalent modifying ions is greater than 30 mole%, the glass tends to crystallize. It is particularly preferred that the content of trivalent modifying ions is in a range of 0 to 25 mole%.

Furthermore, it is preferred that the glass contains 0 to 20 mole% of Hf^{4+} as cations which form the network of the glass. If the content of Hf^{4+} is greater than 20 mole%, then the glass tends to crystallize. It is particularly preferred that the content of Hf^{4+} is in a range of 0 to 15 mole%.

It is preferred that the glass contains 0 to 20 mole% of at least one of Li^{+}, Na^{+} and K^{+} as monovalent modifying ions which have the action of complementing the network structure of the glass. If the content of the monovalent modifying ions is greater than 20 mole%, then the glass tends to crystallize. It is particularly preferred that the content of monovalent modifying ions is in a range of 0 to 10 mole%.

Furthermore, it is preferred that the anions contained in the glass consist of 0 to 20 mole% of Cl^{-} and 80 to 100 mole% of F^{-}. It is possible to improve the stability of the glass against crystallization by the addition of small amounts of Cl^{-}. However, if the content of Cl^{-} exceeds 20 mole%, the chemical durability of the glass becomes poor, and the glass tends to crystallize. It is particularly preferred that the anions of the glass consist of 0 to 10 mole% of Cl^{-} and 90 to 100 mole% of F^{-}.

On the other hand, in the case that the photostimulable luminescence glass is a halogen phosphate glass, the formability characteristic of the glass is further improved by the incorporation of 0.1 to 80 mole% of P^{5+} in the glass in addition to the amounts of each kind of cation of the halide glass described above. If the content of P^{5+} is less than 0.1 mole%, then the effect of improving the formability of the glass is small, and if it exceeds 80 mole%, then the chemical durability of the glass becomes poor. It is particularly preferred that the content of P^{5+} is in a range of 5 to 60 mole%.

In this case, it is preferred that the anions consist of 1 to 95 mole% of O^{2-}, 0 to 20 mole% of Cl^{-} and 5 to 99 mole% of F^{-}. If the content of O^{2-} is less than 1 mole%, then the stability of the glass against crystallization is relatively poor. Conversely, if the content of O^{2-} exceeds 95 mole%, then the emission efficiency is decreased. Furthermore, if the content of Cl^{-} exceeds 20 mole%, then the glass tends to crystallize. It is particularly preferred that the anions in the glass consist of 1 to 50 mole% of O^{2-}, 0 to 10 mole% of Cl^{-} and 40 to 99 mole% of F^{-}.

In the case that the photostimulable luminescence glass is produced from raw materials including Ce^{4+} and/or Eu^{3+}, the glass is melted and shaped in a reducing atmosphere or after addition of a reducing agent such as carbon to the batch. Even in the case that it is produced from raw materials including Ce^{3+} and/or Eu^{2+}, it is preferred that the glass is melted and shaped in an inert or reducing atmosphere in order to prevent oxidation by oxidants remaining in the raw materials. If the glass is melted and shaped in air or in an oxidizing atmosphere, part of the Ce and Eu remain in the glass as Ce^{4+} and Eu^{3+} with a resulting decrease in the concentration of Ce^{3+} and Eu^{2+} which trap positive holes, together with a resulting decrease in the concentration of F-centres etc., which are capable of releasing electrons upon excitation with visible or infra-red light, due to Ce^{4+} which is capable of trapping electrons, whereby the occurrence of photostimulated luminescence is reduced.

Photostimulable luminescence glass prepared in this way displays excellent glass formability, does not tend to crystallize, and can be easily formed into sheets, rods, or fibers etc.. For example, it can be formed into flat sheet glass having dimensions of 400mm x 400mm for use in X-ray photography, wherein complicated process steps can be omitted compared to the preparation of standard polycrystal photostimulable luminescence fluorescence sheets. Furthermore, a clear image is formed by scanning those parts which have been exposed to radiation with a fine laser beam of visible or infrared light, detecting the intensity of the fluorescence generated from each of the exposed parts, and carrying out computer image processing.

Furthermore, a microchannel plate may be constructed by bundling together glass fibers having, for example, an 8 μm diameter core comprised of a glass including Ce^{3+} and/or Eu^{2+} and having a large refractive

index, and a 10µm diameter cladding not including any Ce^{3+} and Eu^{2+} and having a small refractive index. When such a microchannel plate is used, then the fluorescence generated upon exposure to the laser beam is capable of high resolution since there is no leakage to the outside of the fiber and no scattering of light. Furthermore, defects are generated along the whole length of the fiber upon exposure to radiation such as X-rays etc.. When the core of the fiber is exposed to visible or infra-red light in this state, electrons trapped by defects in the core are released and combine with positive holes, the energy thereof excites the Ce^{3+} or Eu^{2+}, and light is generated along the whole core. As a result, the light is detected with high sensitivity.

The present invention will now be described in more detail with reference to the following examples. The scope of the present invention shall not be limited to these examples.

Example 1:

High purity raw materials, CeO_2, SiO_2, Na_2CO_3, Sm_2O_3 were weighed out in proportions required to give a silicate glass having a composition whose cations are made up of 0.9 mole% of Ce^{3+}, 72.6 mole% of Si^{4+}, 25.6 mole% of Na^+ and 0.9 mole% of Sm^{3+}, mixed together and melted in a platinum crucible at 1450°C for 30 minutes, and then subjected to cast forming to obtain a glass. This glass was then placed in a glassy carbon crucible, and subjected to reduction treatment for one hour by heating to 1450°C in an atmosphere of N_2 and 5 vol.% H_2. The melt in each crucible was then quenched to near room temperature.

The thus produced glass was then cut and polished, after which its photostimulated luminescence emission spectrum, stimulation excitation spectrum and afterglow characteristic were measured. The measuring system shown in figure 1 was used to measure the photostimulated luminescence emission spectrum. In this measuring system, the glass sample is exposed to X-rays from a tungsten target at 40kV and 30mA for 600 seconds, followed by exposure to excitation light from a 170µW He-Ne laser (630nm). The fluorescent light generated upon exposure to the He-Ne laser is measured after passing it through a B-410 band pass filter. Blue-colour (about 410nm) photostimulated luminescence was observed.

The measuring system shown in figure 2 was used to measure the stimulation excitation spectrum. In this measuring system, the glass sample was exposed for 1800 seconds to X-rays from a W-target at 40kV and 30mA, and the emission at 410nm was monitored. Light from a halogen lamp (100W) was passed through a spectroscope, and the excitation spectra of the secondary excitation emission was measured. A B-410 band pass filter and interference filter were used on the light-receiving side. As shown in figure 3, the detected photostimulated luminescence excitation spectra had a peak at about 600nm, closely matching the He-Ne laser (633nm). The short wavelength light in figure 3 was leaked light.

As can be seen from figure 4 which shows the afterglow characteristic, it was observed that the emission after exposure to the He-Ne laser dropped off extremely sharply, and was completely quenched within a period of ten seconds. In figure 4, the time-axis for example 1 is slightly shifted to avoid overlap with the data of example 2.

Example 2:

High purity raw materials, CeO_2, B_2O_3 and Na_2CO_3 were weighed out in proportions required to give a borate glass having a composition whose cations are made up of 0.5 mole% of Ce^{3+}, 74.6 mole% of B^{3+} and 24.9 mole% of Na^+, mixed together, and melted in a platinum crucible at a temperature 1100°C for 30 minutes to obtain a glass. This glass was then placed in a carbon crucible, and subjected to reduction treatment for one hour at 1100°C in an atmosphere of N_2 and 5 vol.% H_2. The melt in each crucible was then quenched to near room temperature.

The thus produced glass was then cut and polished, after which its photostimulated luminescence emission spectrum and afterglow characteristic were measured in the same way as example 1. The emitted fluorescent light was measured after passing it through a U-360 band pass filter. Photostimulated luminescence in the ultra-violet region at about 360nm was observed. As shown in figure 4, the afterglow characteristic showed an extremely sharp drop-off.

Example 3:

High purity raw materials CeO_2, SiO_2, Cs_2O_3 were weighed out in proportions required to give a silicate glass having a composition whose cations are made up of 0.15 mole% of Ce^{3+}, 53.76 mole% of Si^{4+} and 46.09 mole% of Cs^+, mixed together and melted in a platinum crucible at 1500°C for 30 minutes, to obtain a glass. This glass was then crushed and placed in a platinum crucible, and then this platinum crucible was placed in an alumina crucible packed with carbon powder. A lid was placed on the alumina crucible, and reduction treatment was carried out for 1 hour at 1550°C in an electric oven heated by a Si-Mo heater. The melt in each crucible was then quenched to near room temperature to obtain a glass.

The glass thus produced was then cut and polished, after which its photostimulated luminescence emission spectrum and afterglow characteristic were measured in the same way as example 1. Blue-colour photostimulated luminescence at about 410nm was observed. The afterglow characteristic also displayed an extremely sharp drop off.

Example 4:

High purity raw materials, CeO_2, B_2O_3, Li_2CO_3, $BaCO_3$ and Al_2O_3 were weighed out in proportions required to give a borate glass having a composition whose cations are made up of 0.05 mole% of Ce^{3+}, 76.49 mole% of B^{3+}, 20.40 mole% of Li^+, 2.04 mole% of Ba^{2+} and 1.02 mole% of Al^{3+}, mixed together and melted in a platinum crucible at 1150°C for 30 minutes, to obtain a glass. This glass was then crushed, placed in a glassy carbon crucible, and subjected to reduction treatment for one hour at 1550°C in an atmosphere of N_2 and 5 vol.% H_2. The melt in each crucible was then quenched to near room temperature.

The thus produced glass was then cut and polished, after which its photostimulated luminescence emission spectrum was measured in the same way as example 2. Photostimulated luminescence in the ultra-violet region at about 360nm was observed.

Example 5

High purity raw materials, CeO_2, SiO_2, Rb_2CO_3, $MgCO_3$ and La_2O_3 were weighed out in proportions required to give a silicate glass having a composition whose cations are made up of 1.53 mole% of Ce^{3+}, 58.44 mole% of Si^{4+}, 38.17 mole% of Rb^+, 0.76 mole% of Mg^{2+} and 1.10 mole% of La^{3+}, mixed together and melted in a platinum crucible at 1550°C for 30 minutes, to obtain a glass. This glass was then crushed, placed in a carbon crucible, and subjected to reduction treatment for one hour at 1550°C in an atmosphere of N_2 and 5 vol.% H_2. The melt in each crucible was then quenched to near room temperature.

The thus produced glass was then cut and polished, after which its photostimulated luminescence emission spectrum was measured in the same way as example 1. Blue-colour photostimulated luminescence at about 410nm was observed.

Example 6

High purity raw materials CeO_2, SiO_2, Na_2CO_3 and Y_2O_3 were weighed out in proportions required to give a silicate glass having a composition whose cations are made up of 0.5 mole% of Ce^{3+}, 80.36 mole% of Si^{4+}, 17.86 mole% of Na^+ and 1.28 mole% of Y^{3+}, mixed together and melted in a platinum crucible at 1500°C for 30 minutes, to obtain a glass. This glass was then crushed, placed in a carbon crucible, and subjected to reduction treatment for one hour at 1500°C in an atmosphere of N_2 and 5 vol.% H_2. The melt in each crucible was then quenched to near room temperature.

The thus produced glass was then cut and polished, after which its photostimulated luminescence emission spectrum was measured in the same way as example 1. Blue-colour photostimulated luminescence at about 410nm was observed.

Example 7:

High purity raw materials Eu_2O_3, B_2O_3, Rb_2CO_3 and Sm_2O_3 were weighed out in proportions required to give a borate glass having a composition whose cations are made up of 0.5 mole% of Eu^{2+}, 89.1 mole% of B^{3+}, 9.9 mole% of Rb^+ and 0.5 mole% of Sm^{3+}, mixed together and melted in a platinum crucible at 1100°C for 30 minutes, to obtain a glass. This glass was then crushed, placed in a glassy carbon crucible, and subjected to reduction treatment for one hour at 1100°C in an atmosphere of N_2 and 5 vol.% H_2. The melt in each crucible was then quenched to near room temperature.

The glass thus produced was then cut and polished, and it was confirmed by standard fluorescence that Eu and Sm were present in the glass in the form of Eu^{2+} and Sm^{3+} respectively. The photostimulated luminescence emission spectrum was measured in the same way as example 1. Blue-colour photostimulated luminescence at about 410nm was observed.

Example 8

High purity raw materials, Eu_2O_3, CeO_2, B_2O_3, SiO_2 and K_2CO_3 were weighed out in proportions required to give a borosilicate glass having a composition whose cations are made up of 0.5 mole% of Eu^{2+}, 0.5 mole% of Ce^{3+}, 71.1 mole% of B^{3+}, 2.5 mole% of Si^{4+} and 25.4 mole% of K^+, mixed together and melted in a platinum crucible at 1100°C for 1 hour, to obtain a glass. This glass was then crushed, placed in a glassy carbon crucible, and subjected to reduction treatment for one hour at 1100°C in an atmosphere of N_2 and 5 vol.% H_2. The melt in each crucible was then quenched to near room temperature.

The glass thus produced was then cut and polished, after which its photostimulated luminescence emission spectrum was measured in the same way as example 1. Blue-colour photostimulated luminescence at about 410nm was observed.

Example 9

High purity raw materials CeO_2, P_2O_5, Al_2O_3 and Na_2CO_3 were weighed out in proportions required to give a phosphate glass having a composition whose cations are made up of 0.05 mole% of Ce^{3+}, 39.98 mole% of P^{3+}, 49.98 mole% of Na^+ and 9.99 mole% of Al^{3+}, mixed together and melted in a platinum crucible at 1250°C for 1 hour, to obtain a glass. This glass was then crushed, placed in a glassy carbon crucible, and subjected to reduction treatment for one hour at 1250°C in an atmosphere of N_2 and 5 vol.% H_2. The melt in each crucible was then quenched to near room temperature.

The glass thus produced was then cut and polished, after which its photostimulated luminescence spectrum was measured in the same way as example 2. Photostimulated luminescence in the ultra-violet region

at about 350nm was observed.

Example 10

High purity raw materials CeO_2, P_2O_5, Al_2O_3, Bi_2O_3 and Na_2CO_3 were weighed out in proportions required to give a phosphate glass having a composition whose cations are made up of 0.05 mole% of Ce^{3+}, 59.97 mole% of P^{3+}, 29.98 mole% of Na^+, 1.00 mole% of Bi^{3+} and 9.00 mole% of Al^{3+}, mixed together and melted in a platinum crucible at 1250°C for 1 hour, to obtain a glass. This glass was then crushed, placed in a glassy carbon crucible, and subjected to reduction treatment for one hour at 1250°C in an atmosphere of N_2 and 5 vol.% H_2. The melt in each crucible was then quenched to near room temperature.

The glass thus produced was then cut and polished, after which its photostimulated luminescence emission spectrum was measured in the same way as example 2. Photostimulated luminescence in the ultraviolet region at about 340nm was observed.

Example 11

High purity raw materials CeO_2, P_2O_5, Al_2O_3, Ga_2O_3, ZnO and Na_2CO_3 were weighed out in proportions required to give a phosphate glass having a composition whose cations are made up of 0.05 mole% of Ce^{3+}, 5.26 mole% of Zn^{2+}, 52.60 mole% of P^{3+}, 31.57 mole% of Na^+, 5.26 mole% of Ga^{3+} and 5.26 mole% of Al^{3+}, mixed together and melted in a platinum crucible at 1250°C for 1 hour, to obtain a glass. This glass was then crushed, placed in a glassy carbon crucible, and subjected to reduction treatment for one hour at 1250°C in an atmosphere of N_2 and 5 vol.% H_2. The melt in each crucible was then quenched to near room temperature.

The glass thus produced was then cut and polished, after which its photostimulated luminescence emission spectrum was measured in the same way as example 2. Photostimulated luminescence in the ultraviolet region at about 340nm was observed.

Example 12

High purity raw materials EuF_2, MgF_2, AlF_3, CaF_2, SrF_2, BaF_2, BaF_2 and YF_3 were weighed out in proportions required to give a glass having a composition whose cations are made up of 0.1 mole% of Eu^{2+}, 35 mole% of Al^{3+}, 10 mole% of Mg^{2+}, 20 mole% of Ca^{2+}, 10 mole% of Sr^{2+}, 10 mole% of Ba^{2+} and 14.9 mole% of Y^{3+}, and whose anions are made up of 100 mole% of F^-, mixed together, and placed in a glassy carbon crucible; all the above was done in a glove box filled with N_2. The mixture was then melted in a nitrogen atmosphere at 1000°C for 1 hour, and then the melt in each crucible was then cooled to near the glass transition temperature T_g.

The glass thus produced was then cut and polished, after which its photostimulated luminescence emission spectrum was measured in the same way as example 1. Blue-colour photostimulated luminescence at about 400nm was observed.

Example 13

High purity raw materials EuF_2, MgF_2, AlF_3, CaF_2, SrF_2, BaF_2, $BaCl_2$ and YF_3 were weighed out in proportions required to give a glass having a composition whose cations are made up of 1 mole% of Eu^{2+}, 35 mole% of Al^{3+}, 10 mole% of Mg^{2+}, 20 mole% of Ca^{2+}, 10 mole% of Sr^{2+}, 10 mole% of Ba^{2+} and 14 mole% of Y^{3+}, and whose anions are made up of 4.1 mole% of Cl^- and 95.9 mole% of F^-, mixed together, and placed in a glassy carbon crucible; all the above was done in a glove box filled with N_2. The mixture was then melted in a nitrogen atmosphere at 1000°C for 1 hour, after which the melt in each crucible was then cooled to near the glass transition temperature T_g.

The thus produced glass was then cut and polished, after which its photostimulated luminescence emission spectrum was measured in the same way as example 1. Blue-colour photostimulated luminescence at about 410nm was observed.

Example 14

High purity raw materials EuF_2, MgF_2, AlF_3, CaF_2, SrF_2, BaF_2 and $Al(PO)_3$ were weighed out in proportions required to give a glass having a composition whose cations are made up of 0.8 mole% of Eu^{2+}, 18.8 mole% of Al^{3+}, 7.7 mole% of Mg^{2+}, 19.3 mole% of Ca^{2+}, 17.8 mole% of Sr^{2+}, 7.7 mole% of Ba^{2+}, and 27.9 mole% of P^{5+}, and whose anions are made up of 36 mole% of O^{2-} and 64 mole% of F^-, mixed together, and placed in a glassy carbon crucible; all the above was done in a glove box filled with N_2. The mixture was then melted in an atmosphere of N_2 and 5vol% H_2 at 1000°C for 1 hour, and then the melt in each crucible was then cooled to near the glass transition temperature T_g.

The thus produced glass was then cut and polished, after which its photostimulated luminescence emission spectrum was measured in the same way as example 1. Blue-colour photostimulated luminescence at about 440nm was observed.

Claims

1. A photostimulable luminescence glass composition which emits fluorescence in the ultra-violet or blue-colour wavelength region when those parts which have been exposed to radiation are excited by visible or infra-red light, and which contains at least one of Ce^{3+} and Eu^{2+} as an active cation.

2. The photostimulable luminescence glass composition according to claim 1 wherein the total amount of at least one of Ce^{3+} and Eu^{2+} is 10 mole% or less

on the basis of all the cations.

3. The photostimulable luminescence glass composition according to claims 1 or 2 wherein the glass is a silicate glass, a borate glass, a phosphate glass, or a mixed oxide glass based on a mixture thereof.

4. The photostimulable luminescence glass composition according to any one of claims 1 to 3 including, as the cations which comprise the glass, 30 to 99 mole% of glass network forming cations, 0 to 70 mole% of glass-network modifying monovalent cations, 0 to 70 mole% of glass-network modifying divalent cations, 0 to 30 mole% of Al^{3+}, and 0 to 40 mole% of glass-network modifying trivalent cations, wherein the percentages are based on the total of all cations.

5. The photostimulable luminescence glass composition according to any one of claims 1 to 4 including, as the cations which comprise the glass, 45 to 95 mole% of glass-network forming cations, 5 to 60 mole% of glass-network modifying monovalent cations, 0 to 40 mole% of glass-network modifying divalent cations, 0 to 10 mole% of Al^{3+}, and 0 to 30 mole% of glass-network modifying trivalent cations, wherein the percentages are based on the total of all cations.

6. The photostimulable luminescence glass composition according to claim 4 or 5, wherein the glass-network forming cations consist of at least one of Si^{4+}, B^{3+} and P^{5+}, the glass-network modifying monovalent cations consist of at least one of Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+} and Tl^{+}, the glass-network modifying divalent cations consist of at least one of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}, and the glass-network modifying trivalent cations consist of at least one of Y^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, Bi^{3+} and Ln^{3+} (where Ln is a rare earth element other than Ce).

7. The photostimulable luminescence glass composition according to claim 1 or 2, wherein the glass composition includes halide ions as the anions.

8. The photostimulable luminescence glass composition according to claims 1, 2 or 7, which is a halide glass including, as the cations which comprise the glass, 10 to 60 mole% of Al^{3+}, 8 to 70 mole% of glass-network modifying divalent cations, 0 to 30 mole% of glass-network modifying trivalent cations, 0 to 20 mole% of Hf^{4+} and 0 to 20 mole% of glass-network modifying monovalent cations, wherein the percentages are based on the total of all cations, and including, as anions which comprise the glass, 0 to 20 mole% of Cl^{-}, and 80 to 100 mole% of F^{-}, wherein the percentages are based on the total of all anions.

9. The photostimulable luminescence glass composition according to claims 1, 2, 7 or 8, which is a halide glass including, as the cations which comprise the glass, 20 to 40 mole% of Al^{3+}, 8 to 60 mole% of glass-network modifying divalent cations, 0 to 25 mole% of glass-network modifying trivalent cations, 0 to 15 mole% of Hf^{4+} and 0 to 10 mole% of glass-network modifying monovalent cations, wherein the percentages are based on the total of all cations, and including, as anions which comprise the glass, 0 to 10 mole% of Cl^{-}, and 90 to 100 mole% of F^{-}, wherein the percentages are based on the total of all anions.

10. The photostimulable luminescence glass composition according to claims 1, 2 or 7, which is a halogen phosphate glass including, as the cations which comprise the glass, 10 to 60 mole% of Al^{3+}, 0.1 to 80 mole% of P^{5+}, 8 to 70 mole% of glass-network modifying divalent cations, 0 to 30 mole% of glass-network modifying trivalent cations, 0 to 20 mole% of Hf^{4+} and 0 to 20 mole% of glass-network modifying monovalent cations, wherein the percentages are based on the total of all cations, and including, as anions which comprise the glass, 1 to 95 mole% of O^{2-}, 0 to 20 mole% of Cl^{-} and 5 to 99 mole% of F^{-}, wherein the percentages are based on the total of all anions.

11. The photostimulable luminescence glass composition according to claims 1, 2, 7 or 10, which is a halogen phosphate glass including, as the cations which comprise the glass, 20 to 40 mole% of Al^{3+}, 5 to 60 mole% of P^{5+}, 8 to 60 mole% of glass-network modifying divalent cations, 0 to 25 mole% of glass-network modifying trivalent cations, 0 to 15 mole% of Hf^{4+} and 0 to 10 mole% of glass-network modifying monovalent cations, wherein the percentages are based on the total of all cations, and including, as anions which comprise the glass, 1 to 50 mole% of O^{2-}, 0 to 10 mole% of Cl^{-} and 40 to 99 mole% of F^{-}, wherein the percentages are based on the total of all anions.

12. The photostimulable luminescence glass composition according to any one of claims 8 to 11, wherein the glass-network modifying divalent cations consist of at least one of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}, the glass-network modifying trivalent cations consist of at least one of Y^{3+} and Ln^{3+} (wherein Ln is a rare earth element other than Ce), and the glass-network modifying monovalent cations consist of at least one of Li^{+}, Na^{+} and K^{+}.

FIG.1

PHOTOSTIMULATED LUMINESCENCE EMISSION SPECTRUM MEASURING SYSTEM

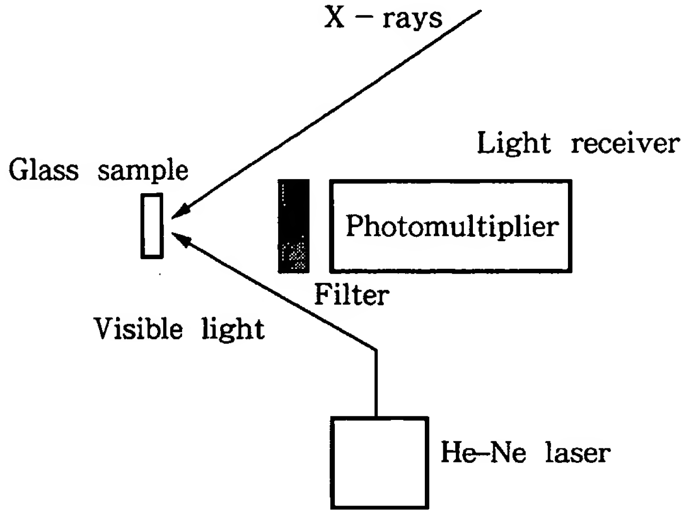


FIG.2

PHOTOSTIMULATED LUMINESCENCE EXCITATION SPECTRUM MEASURING SYSTEM

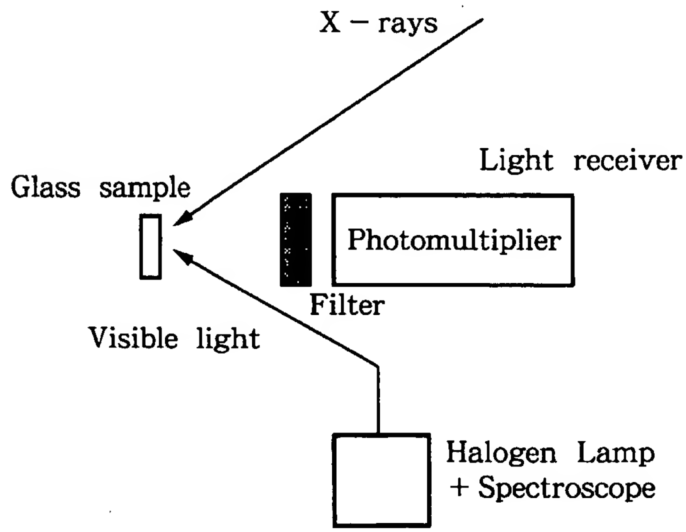


FIG.3

PHOTOSTIMULATED LUMINESCENCE EXCITATION SPECTRUM

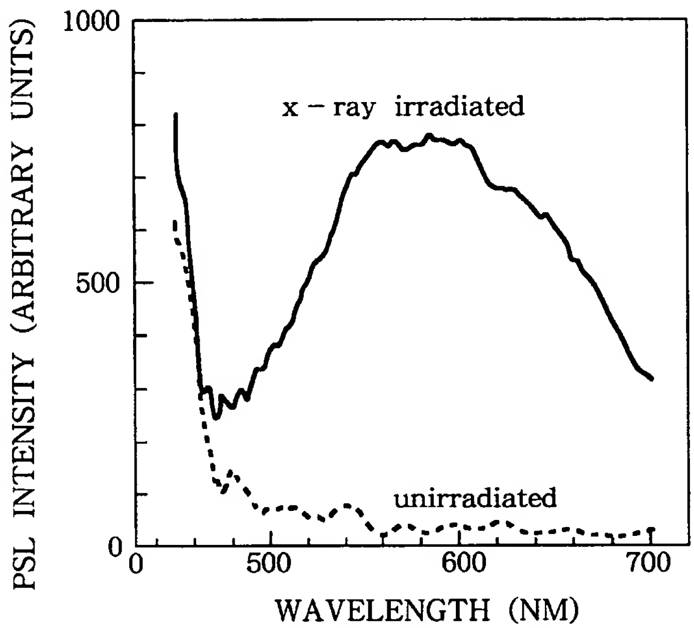
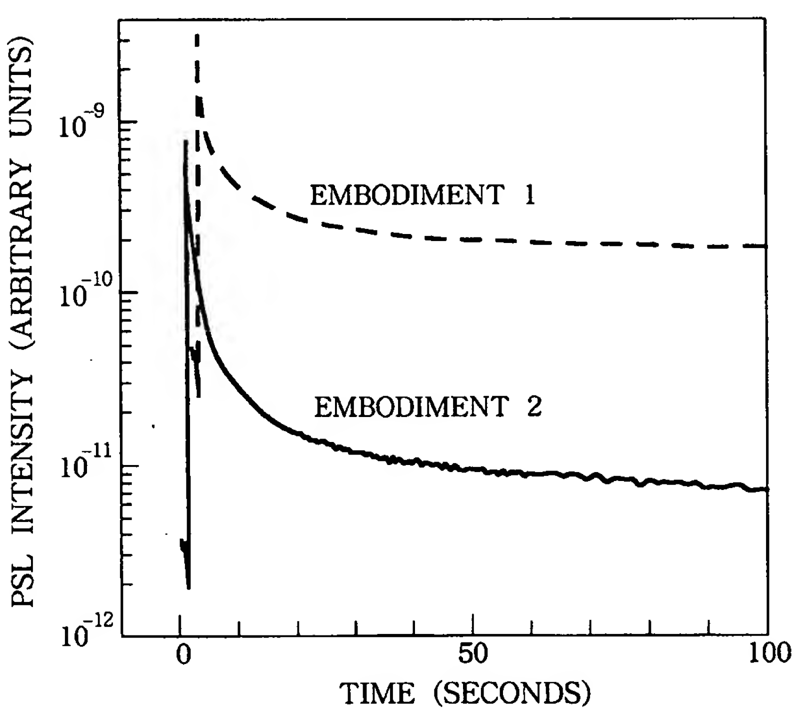


FIG.4

AFTER-GLOW CHARACTERISTIC



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EUROPEAN SEARCH REPORT

Application Number
EP 96 12 0205

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 3 522 191 A (TURNER WARREN H ET AL) 28 July 1970 * the whole document *	1-6	C03C4/00 C03C4/12 C03C3/095 C03C3/15 C03C3/247 C03C3/17 C03C3/32
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X	US 3 032 428 A (GINTHER) 1 May 1962 * the whole document *	1-6	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13 March 1997	Van Bommel, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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Application Number
EP 96 12 0205

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 5107810, KIM I S ET AL: "Airborne alpha emitters monitored by a glass fibre scintillator bundle" XP002027492 * abstract * & ADVANCES IN RADIATION MEASUREMENTS: APPLICATIONS AND RESEARCH NEEDS IN HEALTH PHYSICS AND DOSIMETRY, CHALK RIVER, ONT., CANADA, 3-6 OCT. 1994, vol. 61, no. 1-3, ISSN 0144-8420, RADIATION PROTECTION DOSIMETRY, 1995, UK, pages 77-80, ---	1-6	
X	WO 94 07805 A (LANDA LEONID ;LANDA KSENIA (US)) 14 April 1994 * page 3, last paragraph - page 8 * ---	1-6	
X	US 4 666 870 A (POULAIN MARCEL J ET AL) 19 May 1987 * column 4, line 62 - column 5, line 40; example 22 * ---	1,2,7-9, 12	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
X	EP 0 338 934 A (CENTRE NAT RECH SCIENT) 25 October 1989 * page 1 - page 2 * ---	1-6	
X	EP 0 199 409 A (PHILIPS NV) 29 October 1986 * column 1, line 1 - column 3, line 51; example 14 * -----	1-6	

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